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SONO-PHOTO-DEGRADATION OF CARBAMAZEPINE IN A THIN FALLING FILM REACTOR: OPERATION COSTS IN PILOT PLANT

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ABSTRACT

The photo-Fenton degradation of carbamazepine (CBZ) assisted with ultrasound radiation (US/UV/H₂O₂/Fe) was tested in a lab thin film reactor allowing high TOC removals (89% in 35 minutes). The synergism between the UV process and the sonolytic one was quantified as 55.2%.

To test the applicability of this reactor for industrial purposes, the sono-photo-degradation of CBZ was also tested in a thin film pilot plant reactor and compared with a 28 L UV-C conventional pilot plant and with a solar Collector Parabolic Compound (CPC). At a pilot plant scale, a US/UV/H₂O₂/Fe process reaching 60% of mineralization would cost 2.1 and 3.8 €/m³ for the conventional and thin film plant respectively. The use of ultrasound (US) produces an extra generation of hydroxyl radicals, thus increasing the mineralization rate.

In the solar process, electric consumption accounts for a maximum of 33% of total costs. Thus, for a TOC removal of 80%, the cost of this treatment is about 1.36 €/m³. However, the efficiency of the solar installation decreases in cloudy days and can not be used during night, so that a limited flow rate can be treated.

Keywords: CPC, economics, pilot plant; radicals; ultrasound; UV

1. INTRODUCTION

Process intensification is about providing a chemical process with the precise environment required which results in better products, and processes which are safer, cleaner, smaller and cheaper [1]. Some features include moving from batch to continuous processing, using new emerging technologies (such as ultrasound) and use of intensive reactor technologies with high mixing and heat transfer rates in place of conventional stirred tanks [2, 3].

Regarding the first feature, homogeneous advanced oxidation processes (AOPs) have been largely used to degrade refractory organic pollutants present in water [4-7]. Sonophotocatalysis (consisting of a combination of ultrasonic sound waves, ultraviolet radiation and a catalyst) has recently emerged as an alternative water treatment method [8-10] due to several advantages: lower doses of catalysts and reagents, no need for low turbidity, etc. However, the use of high-frequency ultrasound demands high amounts of energy, so that an economical study is needed to quantify its applicability in each reactor type.

A previous research [11] showed the important contribution of $\bullet\text{OH}$ radicals during degradation of carbamazepine under the US-UV- H_2O_2 -Fe system. Under optimum conditions, mineralization reached 93% in 35 minutes under batch conditions. The authors also performed a study of the flow pattern inside the reactor, showing that improvement in mineralization rate with US radiation could not be attributed to a positive effect in mixing. Thus, the aim of this research is focussed on i) understanding the effect of US radiation on the formation of hydroxyl radicals to improve

mineralization, ii) to perform mineralization tests at a pilot plant scale and iii) to analyze the economic viability of the process

Regarding the use of new reactor technologies and in addition to conventional batch reactors, in the last years several new type of reactors have been developed to remove pollutants from water effluents including thin film reactors and collector parabolic compound (CPC). Thin film reactors have a large heat and mass transfer area per unit liquid volume that make them very efficient in industry. They have low contact time, low pressure drop, and easy cleaning. The main inconvenience is that high flow rates induce waves in the falling liquid and the film can be broken. To avoid this trouble, we can use a smaller tube and ensure the perfect verticality of the tube. The flow in the form of a thin film also favors heat exchange, obtaining larger coefficients [12], in case that heating/cooling is necessary in the system. They are also useful when light penetration is not good in a batch reactor. Unfortunately, they are usually less applied for photochemical reactions.

On the other hand, solar photo-Fenton in a compound parabolic collector (CPC) reactor is known to be one of the most environmentally benign and cost-effective systems for wastewater treatment [13-15].

In this work, a simple experimental falling film pilot plant has been constructed, tested and compared with a conventional artificial UV cylindrical reactor. Thus, results in the thin film device have also been compared with those obtained in a solar CPC plant. Carbamazepine (CBZ), a refractory pharmaceutical organic drug not degraded in WWTP processes (removal efficiencies below 10%) has been treated as a model

pollutant and a previously optimized photo-Fenton process assisted with ultrasound radiation (US/UV/H₂O₂/Fe) has been used as an intensified AOP. The sonophotolytic degradation of organic compounds has already proved to be effective due to the synergistic effect of the US and UV irradiation [16].

In order to determine the efficacy of the thin film reactor approach as a process intensification technology for photocatalytic wastewater treatment, an economical analysis has also been made. There are many studies using thin film reactors with TiO₂ as a heterogeneous wastewater treatment [17-19]. However, to our knowledge no studies have been made in homogeneous phase comparing technical and economical efficiencies.

2. EXPERIMENTAL SET-UP

2.1. Laboratory scale device

The experimental set-up consists on two glass pipes bundled as a shell-and-tube heat exchanger (inner diameter = 2.75cm; length = 28.3 cm). The CBZ solution flows in the form of a thin film that runs down inside the inner tube where a Heraeus UV immersed lamp TNN 15/32 is located. A pump is used to regulate the flow rate. A wider element in the upper part of the column acts as an overflow system which is responsible for the fluid falling as a film. The optical path lengths in this thin film reactor was obtained to be 1.23 cm. Due to the small dimensions of the thin film, it is ensured that all the radiation coming from the lamp is reaching the wastewater, enhancing the efficiency of the reactor.

2.2. Pilot plants

2.2.1. UV-Pilot Plant

The UV pilot plant (FLUORACADUS-08/2.2) is shown in Figure 1 and is composed by a 28 L reactor (2240mm x 730mm x 100mm), with four UV-C lamps (280–200 nm) TUV_TL_D_55W_HO_SLV UV-C PHILIPS. The system is able to treat up to 1400 l/h. Temperature (up to 60°C) is controlled by a digital Fuji PXR4TAY1-1Vcontroller.

2.2.2. CPC Pilot Plant

The CPC consisted of a tank (50 L), a centrifugal recirculation pump, a solar collector unit with an area of 2 m² (concentration factor = 1) in an aluminum frame mounted on a fixed south-facing platform tilted 39° in Ciudad Real (Spain) with connecting tubing and valves. The solar unit had 16 borosilicate glass tubes (OD 32 mm) and the total illuminated volume inside the absorber tubes was 16 L. Visible solar radiation (400-600 nm) and UV radiation (200-400 nm) were measured by two Ecosystem model ACADUS radiometers which provided data for the incident UV-A solar power (W m⁻²) and accumulated solar power (W h).

2.2.3. Thin film pilot plant

This pilot plant has the same configuration that the lab prototype, although now it consists on a two concentric stainless steel tube with higher dimensions (3.8 cm inner diameter; 85 cm height). A 55w submersible lamp (BIO-UV Ultraviolet solutions) was used.

Figure 1

2.3. Experimental runs and analysis

All experiments were carried out at pH =2.7 and 30°C. A 24 kHz, 200 W direct immersion horn sonicator (UP200S with an S14 sonotrode, Hielscher) was used to generate ultrasonic sound waves in the sonoreactor in lab devices. The amplitude of the oscillatory system (power output) can be steplessly adjusted between 20% and 100%. The pulse mode factor (cycles) can be continuously varied between 10% and 100%. The set value equals the acoustic irradiation time in seconds, the difference to 1 s is the pause time. Thus, a setting of 1 implies that it is continuously switched on, whereas a setting of 0.6 means a power discharge of 0.6 s and a pause of 0.4 s. Amplitude and pulse length (cycles) were maintained constant at 60% and 1, respectively according to literature [11].

On the other hand, a UIP 1000HD230 (Hielscher) with a sound protection box was used in pilot plants installations (see Figure S1 in supplementary material). The main characteristics are: ultrasonic frequency of 20kHz, automatic frequency tuning system, amplitude 25 micron adjustable from 50 to 100%, and dry running protected. The dimensions of the transducer are (LxWxH) 435x110x71mm. The generator uses 230 Volts, AC, single phase, 8A, 50-60Hz. A sonotrode (BS2d34) titanium, tip diameter 34mm, length 125mm was used.

Figure S1

More details of reactor configurations and ultrasound power are shown in Table 1. Initial concentration of carbamazepine (CBZ) in deionized water was 78.2 ppm (TOC = 55 ppm). The flow rate was 45 L/h in the thin film lab device, 1140 L/h in the conventional and solar pilot plants and 150 L/h in the thin film plant.

Table 1

CBZ (99%) was obtained from Acros. Analytical grade ferrous sulfate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$), and 30% w/v hydrogen peroxide (H_2O_2) were acquired from Merck. The pH of the wastewater was adjusted with H_2SO_4 and NaOH solutions. Total organic carbon concentration was determined using a TOC analyzer (Shimadzu TOC-5000A).

Quantification of hydroxyl radicals was carried out using disodium salt of terephthalic acid (NaTA) [20]. NaTA (non-fluorescent) is known as an $\text{HO}\cdot$ scavenger; it reacts with $\text{HO}\cdot$ to form 2-hydroxyterephthalic acid (HTA, fluorescent). The concentration of HTA was determined by its fluorescence, which yield is proportional to the $\text{HO}\cdot$ concentration in the solution in the excess of NaTA.

The HTA fluorescence yield was measured with an RF 6000 spectro-fluorophotometer (Shimadzu). The excitation wavelength was set at 315 nm and the fluorescence spectra of the solution were collected in the range of 320 nm - 500 nm. The peak intensity was quantified for each solution at the emission wavelength of 425 nm using a previous calibration.

3. RESULTS AND DISCUSSION

3.1. Study of UV, US and UV/US processes

Figure 2 shows degradation of CBZ under different processes (UV, US and UV/US) for the lab falling film device. The values of the photolytic constant (k_{UV}) were 0.0264 min^{-1} for CBZ degradation and 0.0019 min^{-1} for mineralization. The values of the sonolytic constant (k_{US}) were 0.0044 min^{-1} for CBZ degradation and 0.002 min^{-1} for mineralization. It was proved that hydrogen peroxide was either not formed under these conditions or it was below detection limits.

Figure 2

The synergism between the UV process and the sonolytic one can be quantified using the pseudo first order degradation rate constants according to equation (1) [21]:

$$Synergy (\%) = \frac{k_{UV+US} - (k_{UV} + k_{US})}{k_{UV+US}} \times 100 = \frac{0.0688 - (0.0264 + 0.0044)}{0.0688} \times 100 = 55.23 \quad (1)$$

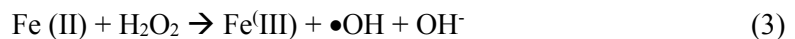
3.2. Determination of optimal operation conditions (US/UV/H₂O₂/Fe)

Figure 3a shows the results for CBZ degradation under different initial H₂O₂ concentrations for the system (US/UV/H₂O₂). CBZ was practically completely removed in all the cases, except for at very low hydrogen peroxide concentration (5 ppm). However TOC removal (Figure 3b) reached a maximum of 46% in 35 minutes when using 20 ppm of H₂O₂. Results also showed that the CBZ degradation rate followed a pseudo-first order rate (Figure 3c) with the pseudo-first order kinetic constant increasing with the initial concentration of H₂O₂ from 0.002 to 0.168 min⁻¹, since more radicals are being formed due to photolysis of hydrogen peroxide:



Figure 3

According to literature [11] when the value of the initial concentration of hydrogen peroxide is increased, HO• radicals may recombine or react according to the “well known” scavenger effect, inhibiting the CBZ degradation rate. Thus, in order to improve mineralization results, 10 ppm of Fe(II) were added to the system. Then, the mineralization degree increases up to 89% in 35 minutes via generation of extra radicals according to the following reaction:

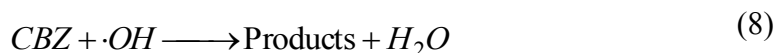
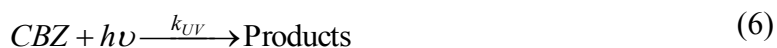
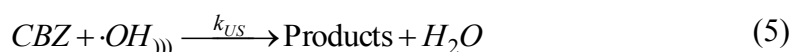


The kinetic mineralization constant, as shown in Figure 3c, increases more than four times, up to 0.075 min⁻¹. Under these selected conditions, the whole study outlined next was developed.

3.3. Study of radicals

Monteagudo et al. [22] studied the sono-photo-Fenton degradation of reactive Blue-4, showing the importance of the different mechanisms. Radical reaction was found to be the main mineralization pathway (93.60%), being the contribution of ultrasonically generated oxidative species to the overall mineralization very low (1.92%). Thus any improvement in the use of US radiation must be related to the radicals involved in mineralization.

The main reactions involved in the sono-photo-Fenton degradation are equations (2) to (8) [23]:



where US denotes the ultrasonic waves, the subscript US denotes the products generated by US and $(\cdot X)$ denotes all the possible intermediates leading to forming H₂O₂.

Figure 4 shows a study of the evolution of the concentration of CBZ and hydroxyl radicals during reaction for different processes at lab scale including: H₂O₂, Fenton (H₂O₂/Fe), photo-Fenton (UV/H₂O₂/Fe) and sono-photo-Fenton (US/UV/H₂O₂/Fe).

Hydrogen peroxide and Fenton system allow a low degradation of initial CBZ (6% and 22% respectively), correlated with the concentration of HO• radicals found in solution (Figure 4b). As expected, the photo-Fenton process improves significantly the CBZ degradation due to generation of extra hydroxyl radicals via reaction (2). Finally, it can be seen that the sono-photo-Fenton process is the fastest degradation process. The amount of hydroxyl radicals is slightly higher at the beginning of reaction, favoring CBZ degradation and later mineralization. This fact confirms that the radical reaction is the main mineralization pathway.

Figure 4

3.3. Comparing pilot plant devices: economical study

At an industrial scale, high flowrates of effluents must be treated, so that pilot plant tests are necessary to confirm the above preliminary results. To this end, three pilot plants were selected: a) thin film, b) a 28 L reactor with four UV-C lamps working as two concentric tubes in continuous mode and c) a solar compound parabolic collector (CPC) plant with an area of 2 m² in order to reduce costs coming from electricity.

Figure 5a shows the results for TOC degradation in both the UV classical pilot plant and the thin film one. Reactor configurations are summarized in Table 1. 70 % of TOC is removed in the thin film photo-reactor and 90% in the classical pilot plant after 2.5 hours. However, the classical UV plant uses a higher amount of energy, since four lamps are being used. An economical approach is thus needed to evaluate the possible application of a thin film device at an industrial scale.

Figure 5

To this end, prices of materials (reagents and catalyst) and electrical consumption of the different devices used for calculation of costs are shown in Table 2, whereas Table 3 summarizes the amount of reagents and catalysts consumed in each processes.

Table 2, Table 3

The whole economic analysis was carried out considering the mineralization process. Figure 5b shows operation costs both for the thin film and the UV classical pilot plant in terms of Euros per cubic meter of treated water. It is confirmed that costs increases when high percentages of TOC removal are needed in both processes, and dramatically increases for removals > 80%. Usually, a complete mineralization is not required and advanced oxidation processes (AOPs) can be designed with the subsequent biological treatment process that treats products from AOPs [24]. Thus, for a 60% of mineralization, costs would raise to 2.1 and 3.8 €/m³ for the UV-classical and thin film plant respectively. However, electricity costs account for the 70 % (thin film) and 50% (classical device) of total cost (Figure 5c). In order to reduce electricity costs for their possible use in an industrial application, the following new experiments were performed:

- a) due to the high power consumption cost of the US probe, new tests were made with the former pilot plants under the photo-Fenton system (UV/H₂O₂/Fe) without US radiation (for the case that operation time is not decisive; otherwise the use of US is mandatory)
- b) substitution of artificial UV radiation with solar energy. Thus, a solar CPC pilot plant was used and compared with the previous results. In this case, oxalic acid was added to the system (mole ratio Fe:(COOH)₂ =3) to form ferrioxalates and improve degradation rate due to generation of Fe(II) through a well-known

mechanism [8]. Moreover, the use of ferrioxalates implies that a higher portion of the solar spectrum can be used.

When experiments without US are analyzed (Figure 6a), the time needed to reach the same mineralization degree increases, as previously explained due to the reduction in hydroxyl radicals available for mineralization of CBZ. For example, for 70 % of TOC removal, ~5.5 hours are now needed in the thin film photo-reactor (~2.5 hours with US), whereas 95 min are employed in the UV conventional plant (40 min with US). However, although the process is clearly faster with US and in the conventional UV pilot plant, the cost study (Figure 6b) indicates that now the thin film device is competitive compared to the UV conventional plant (please note that the thin film plant has just one 55W lamp, whereas the conventional one uses four of them). Costs around 2 €/m³ are obtained in both systems for a 50% of TOC removal.

Figure 6

Regarding the solar process, and in order to compare experiments over several days, it is necessary to use a simple equation to normalize the data so that the time used in Figures comes from the following correlation [25]:

$$t_{30W,n} = t_{30W,n-1} + \Delta t_n \frac{UV}{30} \frac{V_i}{V_T}; \Delta t_n = t_n - t_{n-1}; t_0 = 0 \quad (n=1) \quad (9)$$

where t_n is the experimental time for each sample, UV is the average solar ultraviolet radiation ($\lambda < 400$ nm) measured between t_{n-1} and t_n , and t_{30W} is a normalized illumination time that refers to a constant solar power of 30 Wm⁻² (typical solar UV radiation on a perfectly sunny day around noon). V_T is the total reactor volume and V_i is the total irradiated volume.

The solar process is definitively faster during the first 30 minutes as shown in Figure 6a (70% of mineralization in 16 min). Then mineralization is slower because most of hydrogen peroxide in solution has been consumed. Also costs per unit of volume of water treated are considerably lower as seen in Figure 6b (around 1.3 €/m³ up to 80 % of mineralization). This is due to the low electric consumption that in the CPC pilot plant accounts for 2-33% of total costs, whereas it varies from 60-90% in the thin film device and from 5-61% in the conventional UV plant depending on the desired mineralization degree (Figure 7).

Figure 7

However, the efficiency of the solar installation decreases in cloudy days and it cannot be used during the night, so that a limited flow rate of effluent can be treated, unless a mixed installation including artificial UV lamps is used.

Finally, Figure 8 shows that operation cost (€/g TOC removed) gradually decreases as TOC removal is higher for the three pilot plants studied. In this way we fully benefit from the reagents that are added in one go at the beginning of the process.

Figure 8

Note that this study intends to be an initial guide only. A bigger thin film plant should be tested to confirm these preliminary results. For this reason, only operation costs have been estimated; the investment cost, the salvage value, the estimated useful life, depreciation expense for year and maintenance are not considered here.

Obviously, the concentration of pollutants reaching a Waste Water Treatment Plant (WTP) would be lower than the one treated here and the oxidation processes could be used as a primary step before the biological process, so that very high mineralization

degrees would not be required. The operational costs obtained here could then be decreased at an industrial scale and when taking into account all these considerations. Also, the use of photovoltaic panels could decrease costs when using CPC devices [26].

4. CONCLUSIONS

- An important synergistic effect between sonolysis and UV irradiation of 55.2% was quantified using the first order rate constants for carbamazepine degradation.
- At a pilot plant scale, a US/UV/H₂O₂/Fe process reaching 60% of mineralization would cost 2.1 and 3.8 €/m³ for the conventional and thin film plant respectively. The use of US makes the process faster, due to extra hydroxyl radicals generated, but more expensive.
- At a pilot plant scale under a UV/H₂O₂/Fe process, both the thin film device and the UV conventional plant are comparable in terms of operational costs (~ 2 €/m³ for a 50% of TOC).
- The solar process is faster and cheaper (around 1.3 €/m³ up to 80 % of mineralization), since electric consumption accounts for a maximum of 33% of total costs. However, the efficiency of the solar installation decreases in cloudy days and cannot be used during the night, so that a mixed installation including artificial UV lamps must be used if high flowrates have to be treated.

5. ACKNOWLEDGEMENTS

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FIGURE CAPTIONS

Figure 1. Pilot plant devices. a) Thin film (units in mm); b) conventional UV reactor; c) Solar CPC .

Figure 2. Synergic effect of UV and US on CBZ degradation at the lab thin film device. a) Degradation of CBZ. b) Calculation of kinetic constants

Figure 3. Experiments under US/UV/H₂O₂ and US/UV/H₂O₂/Fe systems. a) Evolution of CBZ degradation; b) evolution of TOC degradation; c) Fitting of pseudo first-order mineralization constants

Figure 4. Formation of hydroxyl radicals under different processes. (Conditions: [H₂O₂] = 20 ppm; [Fe(II)] = 10 ppm). a) CBZ degradation; b) Evolution of hydroxyl radicals.

Figure 5. Comparison of different pilot plants for the US/UV/H₂O₂/Fe process. a) TOC decrease; b) Operation costs per m³ of treated water vs mineralization degree; c) Main component of costs in each process for a 60 % of mineralization.

Figure 6. Comparison of different pilot plants for the UV/H₂O₂/Fe process. a) TOC decrease; b) Operation costs per m³ of treated water vs mineralization degree.

Figure 7. Operational costs (reagents and electricity) vs TOC removal. a) Thin film; b) Conventional UV pilot plant; c) Solar CPC. (Process: UV/H₂O₂/Fe)

Figure 8. Operation costs per g of TOC removed for each process as a function mineralization degree for pilot plants. (Process: UV/H₂O₂/Fe)

Table 1. Reactor configurations and mineralization results.

REACTOR	Volume (l)	Nominal UV power (W)	Measured UV power (W)	US (W)	Mineralization degree (%) and time needed (min)	
	Laboratory device					
Thin film	0.43	15	23.2	168.5	90.0	35
	Pilot plant devices with US					
Conventional UV Pilot plant	33	55×4	208.4	387.8	87.0	120
Thin film		55	51.8		71.6	150
	Pilot plant devices without US					
Solar CPC	33	--	--	--	80.6	25.9
Conventional UV Pilot plant		55×4	208.4		76.7	120
Thin film		55	51.8		77.2	360

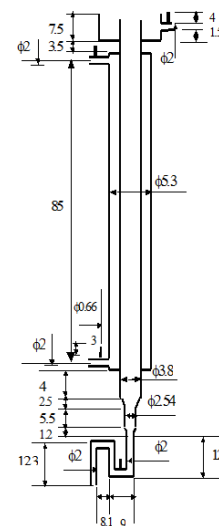
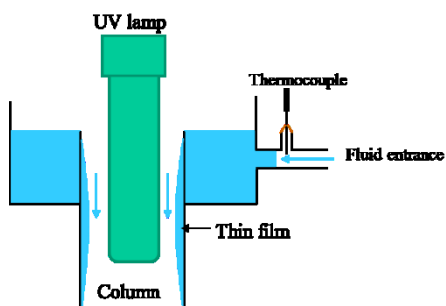
Table 2. Electric power and prices of electricity and reagents

ELECTRIC POWER	
<i>UV Pilot plant*</i>	
Lamps	0.208 kW
Pump	0.050 kW
pH-meter	0.006 kW
Sonotrode	0.387 kW
<i>Solar CPC pilot plant*</i>	
Pump	0.050 kW
pH-meter	0.006 kW
<i>Thin Film pilot plant*</i>	
Pump	0.050 kW
Lamp	0.0518 kW
pH-meter	0.006 kW
Sonotrode	0.387 kW
ENERGY PRICE (industrial rate) [UNESA, 2011]	
0,09122 €/kWh	
REAGENTS PRICES	
Hydrogen peroxide	0,445 €/L
Iron (II) sulphate	0,75 €/kg
Oxalic acid	2,6 €/kg
Sulphuric acid	0,183 €/L

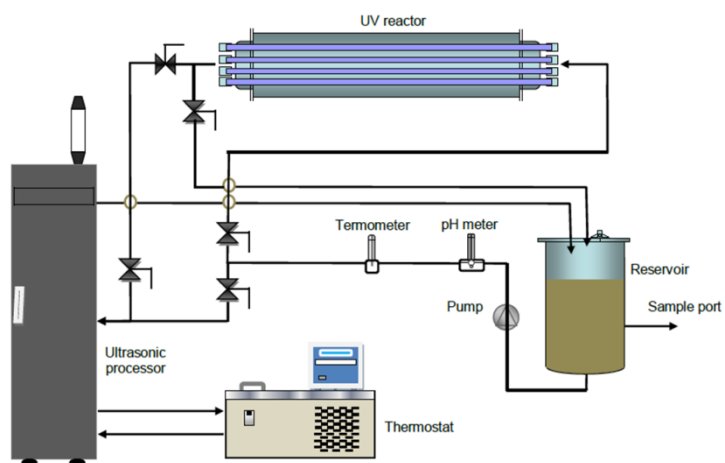
** consumption of some components like signal transformers has not been estimated due to its low value*

Table 3. Amount of reagents consumed in each pilot plant

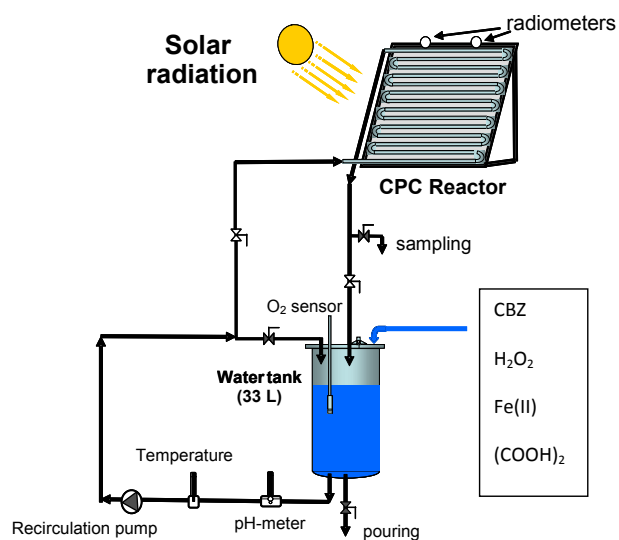
	Conventional UV	Solar CPC	Thin film
Volume of water treated (L)	33	33	33
H ₂ O ₂ (L)	0.075	0.075	0.075
FeSO ₄ (II) (g)	1.64	1.64	1.64
H ₂ C ₂ O ₄ (g)	-	-	1.38
H ₂ SO ₄ (L)	0.013	0.012	0.011



a)

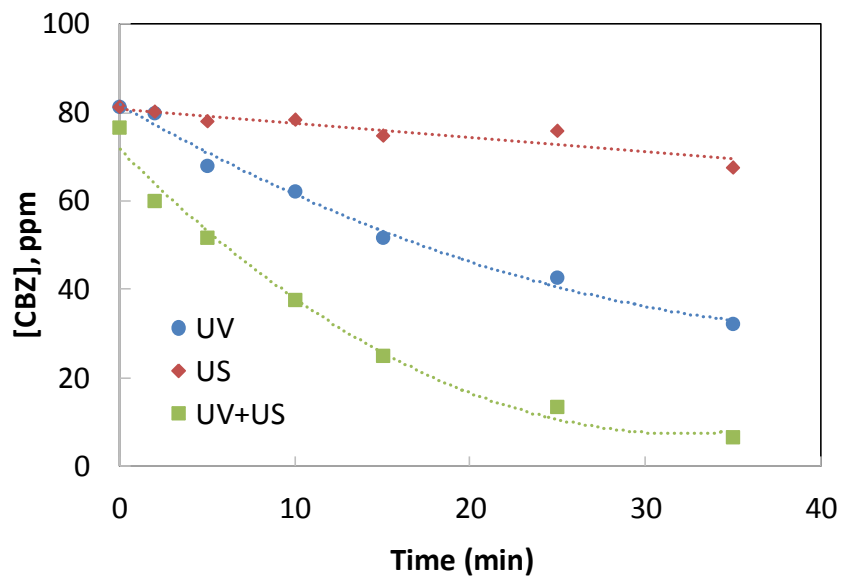


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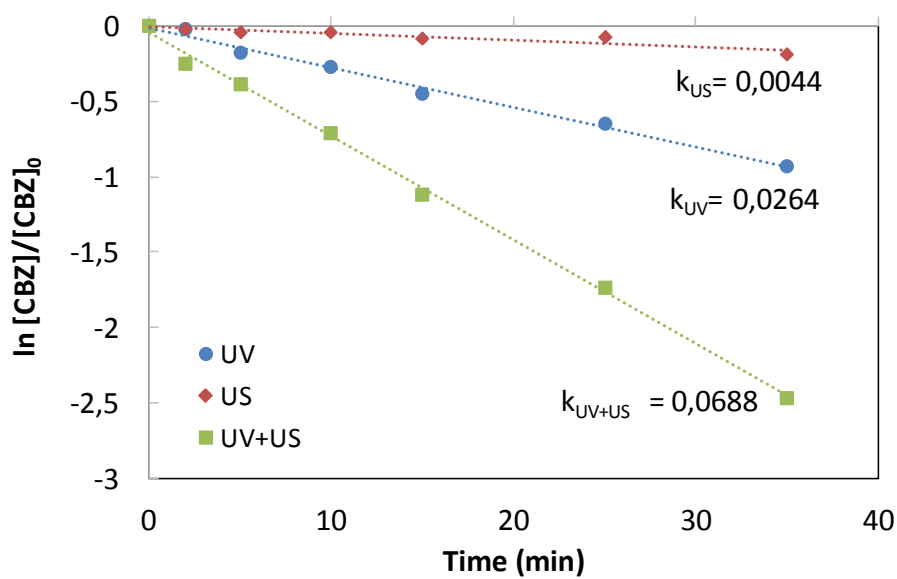


c)

FIGURE 1

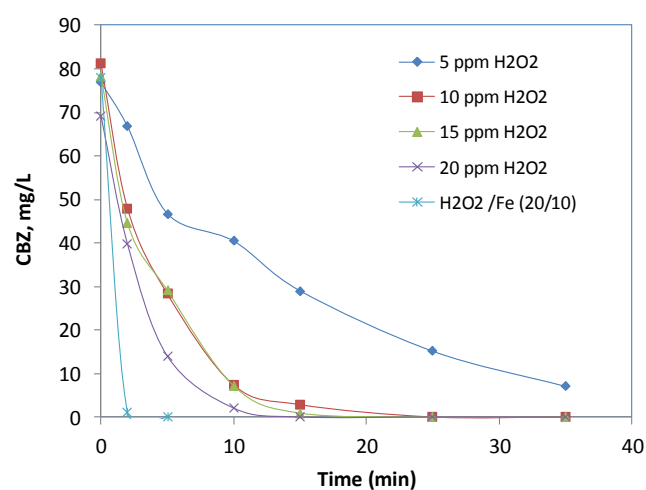


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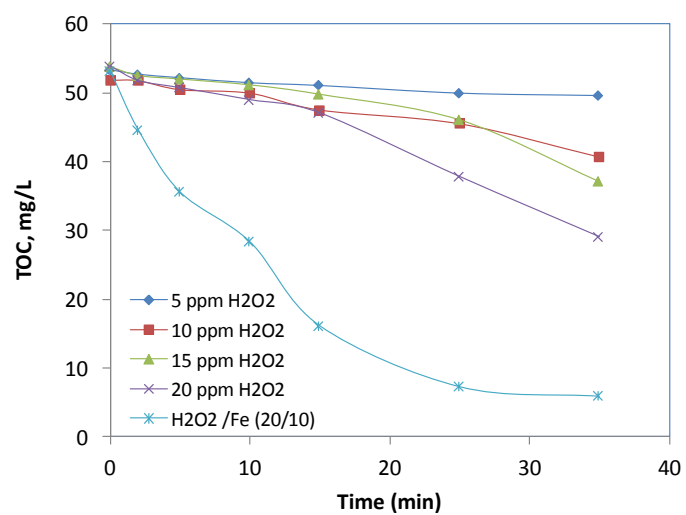


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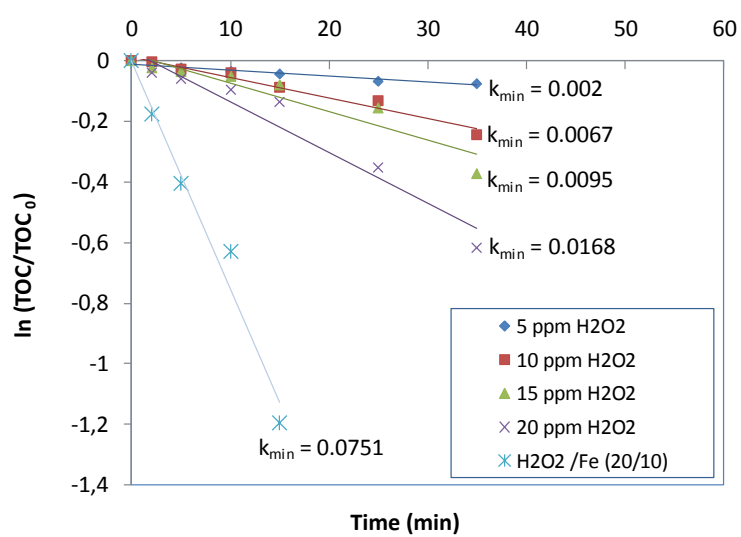
FIGURE 2



a)

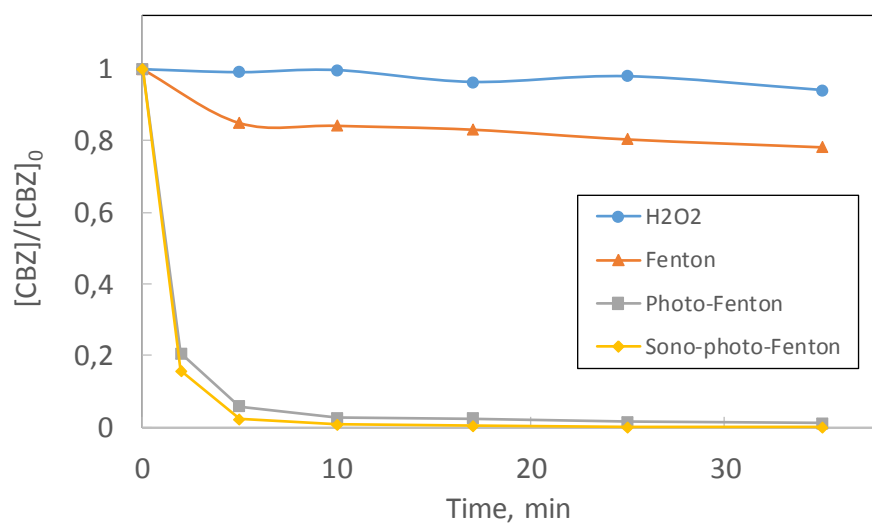


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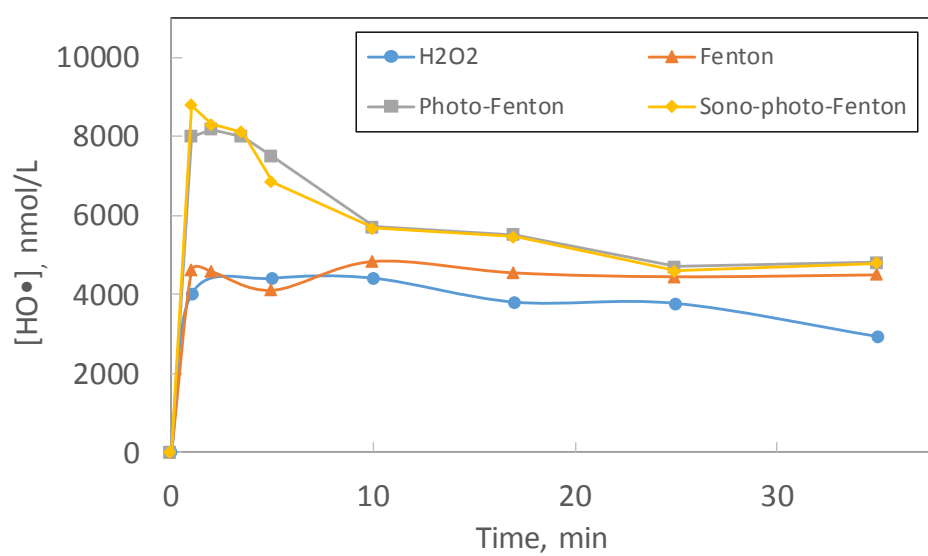


c)

FIGURE 3

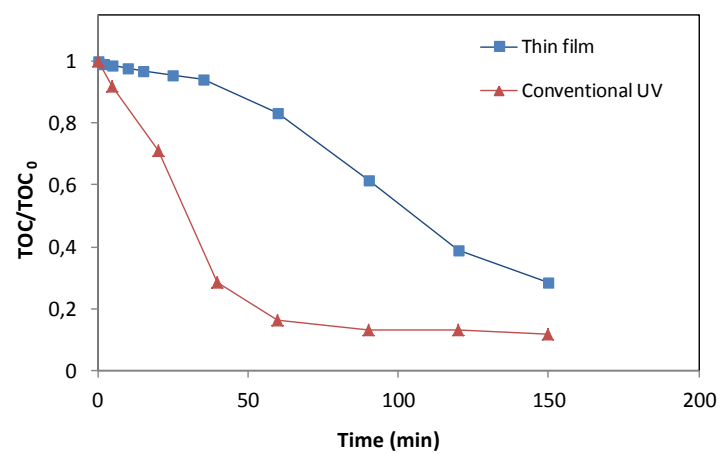


a)

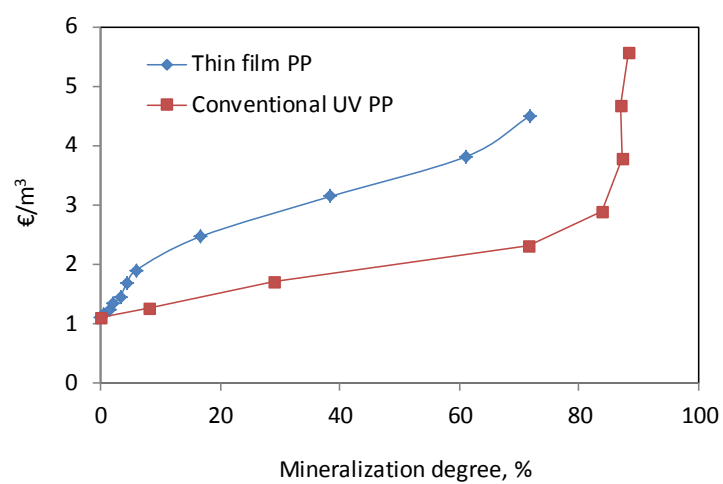


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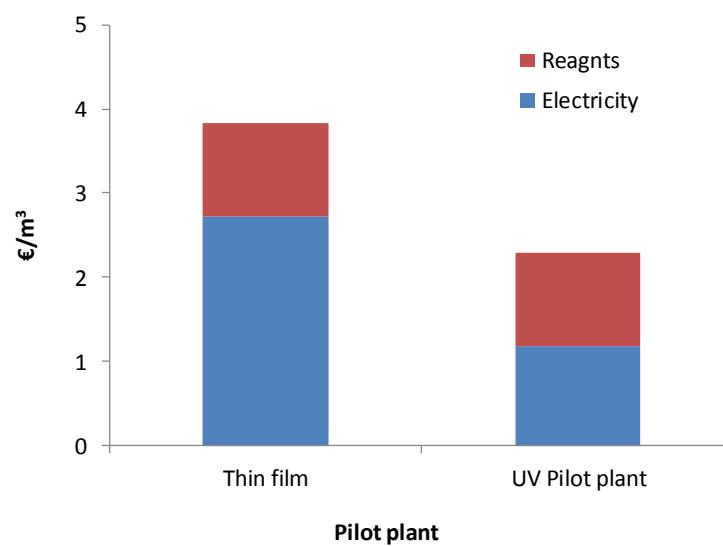
FIGURE 4



a)

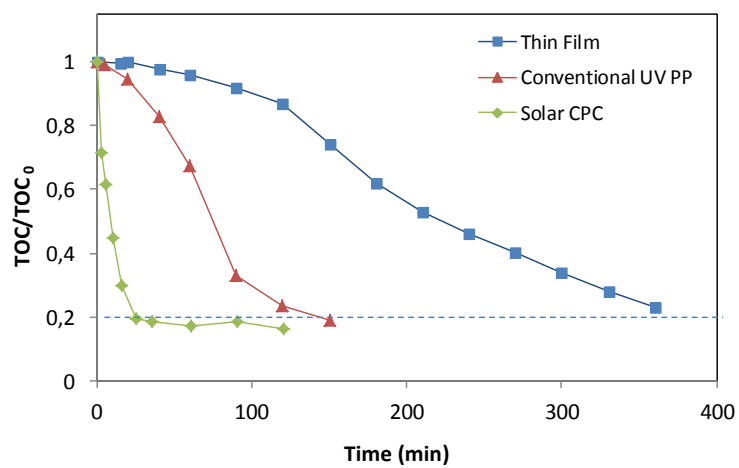


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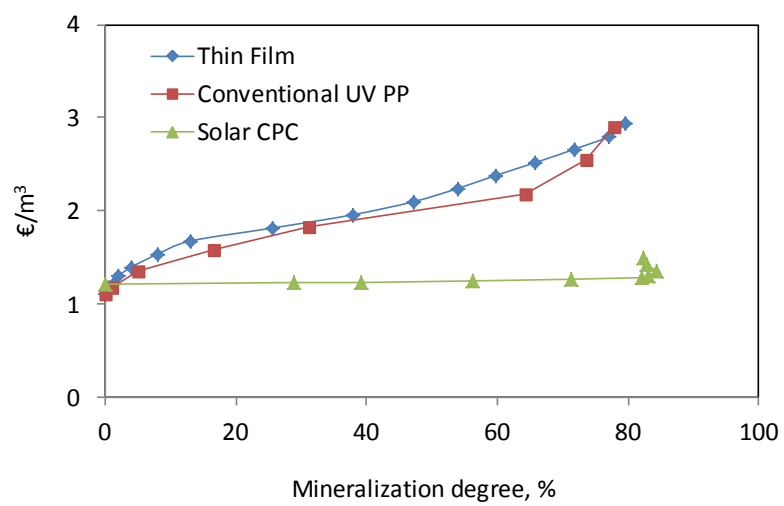


c)

FIGURE 5

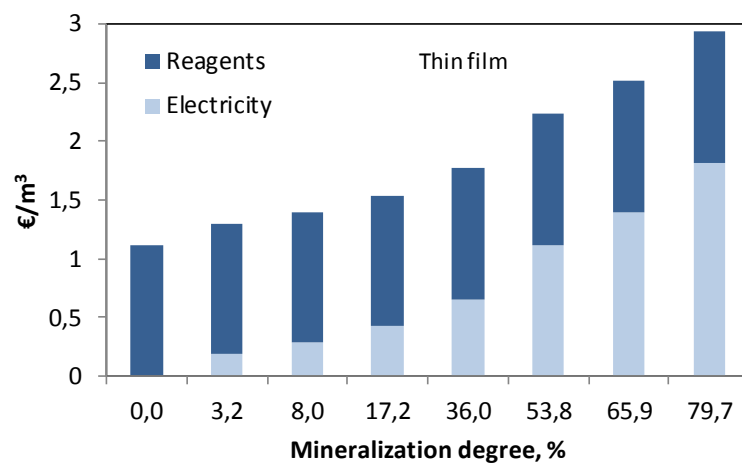


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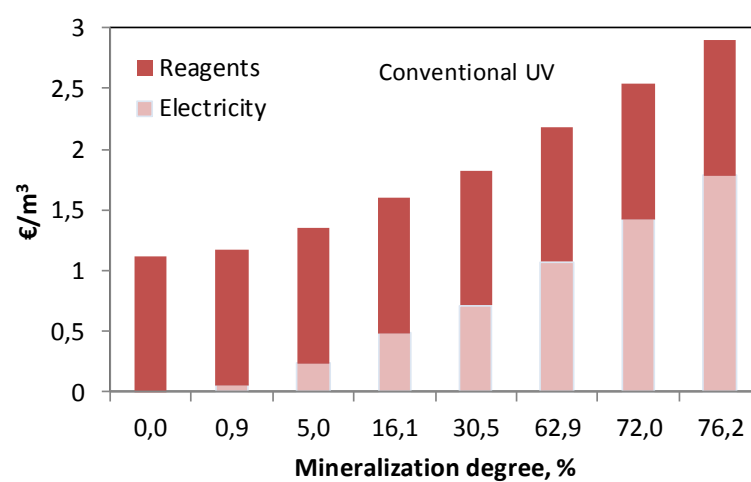


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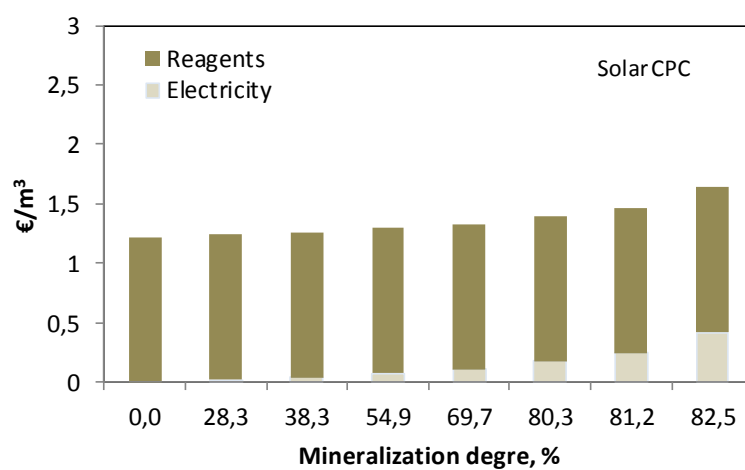
FIGURE 6



a)



b)



c)

FIGURE 7

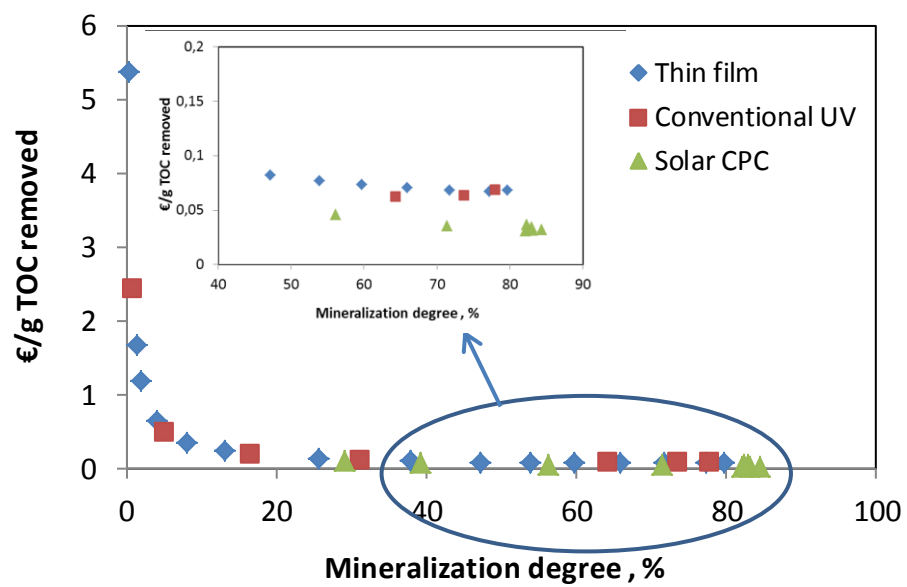


FIGURE 8